Effects of Deuterium Treatments on the Optical Properties of Fused Silica

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Flame produced fused silica, the process used by all American manufacturers, contains a large amount of OH⁻. The fundamental OH⁻ vibration in SiO_2 is at 2.75 μm and its first overtone is at 1.38 μm. Much of the optical absorption at 1.3 μm is due to the wing of the 1.38 μm absorption band. Stone and Burrus[1] described a deuterium treatment given optical fibers to transform the OH⁻ absorption to OD⁻ whose fundamental is at 3.72 μm and first overtone at 1.85 μm. Here we describe some related treatments given to Suprasil II window samples. Spectral traces show that the 1.38 μm absorption peak is diminished while a new absorption peak appears at 1.85 μm. Similar changes appear in the spectrum between 2 and 4 μm. 1.3 μm laser rate calorimetry performed before and after treatment on the sample showing the most complete H↔D exchange exhibited a drop in absorption value to about 1/5. Thus we conclude that over 80% of the optical absorption in Suprasil II at 1.3 μm is due to the OH⁻ molecule. The method offers a way of improving the performance of flame produced fused silica windows used at 1.3 μm.

Key words: fused silica; hydrogen-deuterium exchange treatments; OD⁻ absorption bands; OH⁻ absorption bands; 1.3 μm optical absorption; SiO_2.

1. Introduction

Most types of commercially available fused silica are prepared in a natural gas flame which introduces water into the molecular structure. This appears predominately in the form of an OH⁻ ion. The fundamental OH⁻ vibration ν_3 in SiO_2 is at 2.75 μm. The first overtone $2\nu_3$ of this line appears at 1.38 μm; the second, $3\nu_3$ is at 0.95 μm. A combination tone, $2\nu_3+\nu_1$, where ν_1 is a vibration frequency of SiO_4, occurs at 1.24 μm. The 1.38 and 2.75 μm lines are intense. The wing of the 1.38 μm line contributes an appreciable fraction of the optical absorption measured at 1.3 μm. Thus to obtain low absorbing fused silica at 1.3 μm it is desirable to eliminate or change to another wavelength the absorption band at 1.38 μm. Fused silica produced in a moisture-free plasma arc is free of this absorption band. There is no American manufacturer currently using this process. A German manufacturer charges about twelve times more for plasma arc produced fused silica over flame produced. Thus it would be desirable to investigate treatments of flame produced fused silica to cut down this 1.38 μm absorption.

This water band problem also plagues fabricators of fused silica optical fibers which operate at 1.3 μm. A solution to this problem was presented by J. Stone and C. A. Burrus[1]. The fiber is placed in a deuterium, D_2, atmosphere and heated. Appreciable diffusion of D_2 into silica occurs for temperatures greater than 200°C and 1 atmosphere pressure. The existing OH⁻ ions are converted to OD⁻ ions, changing the locations of the absorption bands. OH⁻ ⇄ OD⁻ ion exchange was found to be complete in a 110 μm (0.004") diameter fiber in less than 3 minutes at 1000°C and 1 atmosphere.

A two atom harmonic oscillator has vibrational frequencies proportional to $\sqrt{\frac{1}{m_1} + \frac{1}{m_2}}$. Thus the wavelength is proportional to $\sqrt{m_1 m_2 / (m_1 + m_2)}$. If $m_1 = 16$, the mass of oxygen, and $m_2 = 1$ or 2, the masses of a hydrogen or deuterium atom, the ratio of the respective wavelengths is $\sqrt{2 \times 17 / 1 \times 18}$ = 1.37. The experimental results confirm that the harmonic oscillator is a good approximation.

2. Experimental Results

Since we had a number of Suprasil II window samples which exhibited a large absorption band near 1.38 μm, had cylinders of D_2 gas for the DF laser, and a pressure bomb-furnace apparatus, some

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[1] Figures in brackets indicate the literature references at the end of this paper.

preliminary attempts were made to see if the above described process could be scaled to sample dimensions on the order of centimeters. Several samples were treated as described in Table 1. This table also lists the % absorption of the 1.38 μm dip before and after treatment. Figure 1 shows the peak before treatment and afterwards on Sample AFML #3208. Note the peak at 1.38 μm

Table 1. Description of D_2 Treatments

Specimen AFML No.	Deuterium Treatment Condition	Observations	% Abs. at 1.38 μm		$\beta_{slope} \div 10^{-3}$
			Before	After Treatment	@ 1.3μm After Treatment
3191	Treated at 1000°C for 24 hrs. at 1 atm. D_2 pressure. Flow rate of D_2 maintained at 0.5 liter/min.	Specimen crystallized surface. Crystallized surface removed before optical meas. The crystalline phase was melanophlogite.	9	7	2.67
3249	Specimen saturated with D_2 at 100 psi at room temperature for 24 hrs. The reaction chamber was then heated up to 900°C and the temperature was maintained for 8 hrs. D_2 pressure was maintained at 100 psi. Graphite coated to prevent crystallization.	No surface crystallization. Spectra traces made without surface polishing. Polished before calorimetry measurements to remove traces of graphite.	8.8	6	2.38
3227	Specimen saturated with D_2 at 150 psi at room temperature for 60 hrs. The reaction chamber was heated to 900°C and temperature was maintained for 6 hrs. 150 psi. Graphite coated to prevent crystallization.	No surface crystallization. Spectral traces made without surface polishing. Polished before calorimetry measurements to remove traces of graphite.	8.5	6	2.21
3208	Specimen treated at 900°C and 150 psi for 26 hrs.	No surface crystallization. Optical measurements carried out without surface polishing.	8.5	3.2	1.65
3237	Specimen treated at 900°C and 150 psi for 104 hrs.	No surface crystallization. Optical measurements carried out without surface polishing.	-	0.8	0.546

decreases while a peak at 1.85 μm appears. Table 1 also lists the result of laser rate calorimetry at 1.3 μm after treatment on these samples. The first three samples were repolished before measurement since they had graphite coatings before being put in the furnace. Samples 3249 and 3227 were also measured before repolishing and had β_{slopes} of 10.5 and 23.4x10^{-3}cm^{-1} indicating evidence of residual amounts of graphite. Samples from this batch of Suprasil II have shown to be reasonably homogeneous. Five other samples were measured while the treatments were made and yielded an average β_{slope} = 2.99x10^{-3} cm^{-1}. Thus the last two treatments did significantly reduce the absorption of the ±0.21

windows at 1.3 μm. The measured β_{slope} on the most thoroughly treated sample being 18% of the untreated value.

One question we have yet to resolve is the permanence of the treatments. Figure 2 shows a trace of AFML 3227 within a day after the treatment, a run one-month later and a run six months later. There seems to be no change. Further work will have to be done on this problem to check its practicality. For example heat the sample with a high power laser beam while in a moist atmosphere.
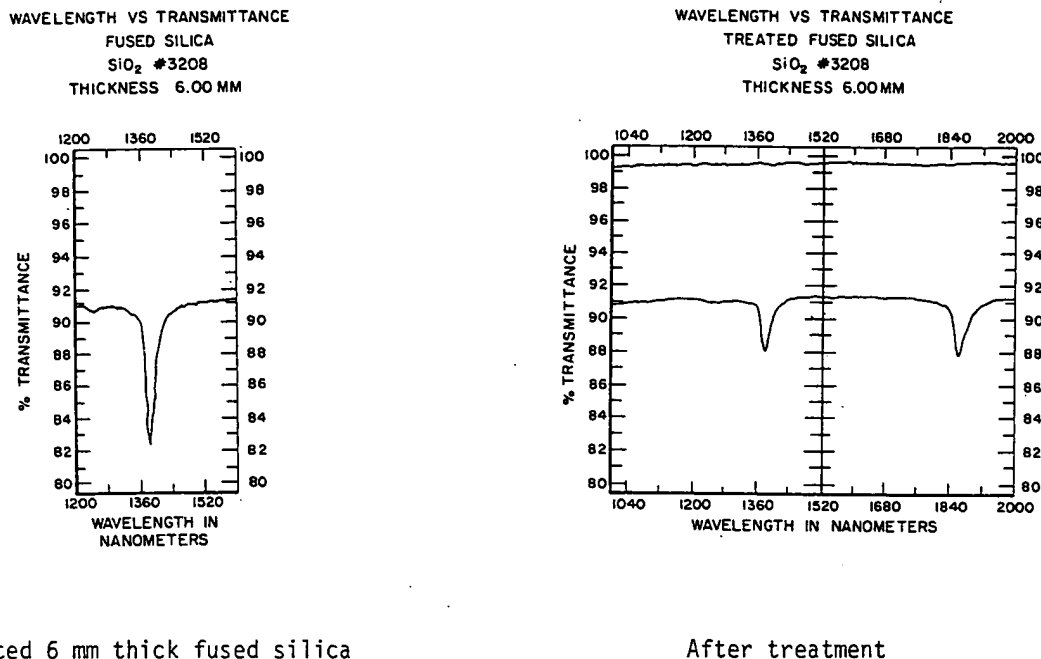
WAVELENGTH VS TRANSMITTANCE
FUSED SILICA
SiO_2 #3208
THICKNESS 6.00 MM

WAVELENGTH VS TRANSMITTANCE
TREATED FUSED SILICA
SiO_2 #3208
THICKNESS 6.00 MM

Untreated 6 mm thick fused silica   After treatment

Figure 1. Beckman 5270 spectral traces of AFML #3208 before and after treatment on an expanded scale in the 1.2-1.6 μm region.

As mentioned earlier there are other OH^- absorption bands. The paper by P. Kaiser et al.[2] lists a number of these bands. Table 2 lists the overtones and combinational vibrations in fused silica, the relative loss caused by them and the wavelength at which they occur for OH^- and OD^-. For a material the transmitted divided by the incident intensity, $I/I_0 = e^{-\beta L}$ where β is the optical absorption coefficient. Hence $\log_{10} I/I_0 = -\beta L \log_{10} e$ or

$$\beta = \frac{2.303 \log_{10} I_0/I}{L}$$

From the Radio Amateur's Handbook, $db \equiv 10 \log_{10}\frac{P_0}{P}$, thus

$$\beta \frac{(db)}{km} \times 2.303 \times 10^{-6} = \beta \ (cm^{-1}).$$

An example of $OH^- \rightarrow OD^-$ conversion is shown in Figs. 1 and 3 where the 1.38 μm decreases in intensity with treatment while the 1.85 μm appears and increases in size. Further examples are listed in Table 2 and are shown in Figure 3.

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WAVELENGTH vs. TRANSMITTANCE
TREATED FUSED SILICA
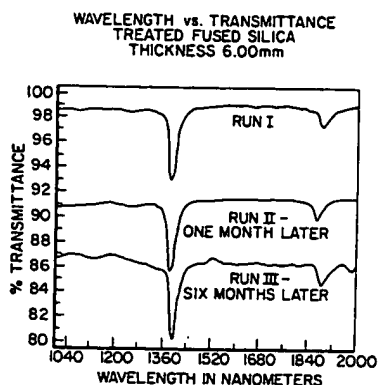**THICKNESS 6.00mm**

Figure 2. Transmission spectra from specimen #3227 after deuterium treatment, one month later and six months later. Run I vertically displaced upward by 8 percent for clarity. Run III vertically displaced downward by 4 percent.

Table 2. Overtones and Combinational Vibrations of OH^- and OD^- in Fused Silica and Relative Peak Intensities

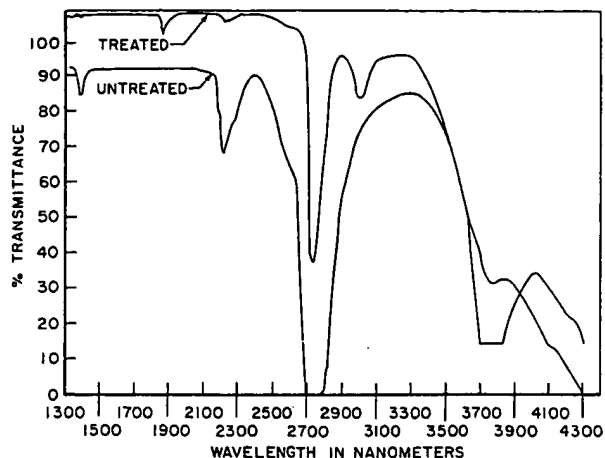| Frequency	Loss cm^{-1}	Wavelength in μm	
		OH^-	OD^-
$5\nu_3^1$	0.0000138	0.60	
$2\nu_1+4\nu_3^1$	0.00000230	0.64	
$\nu_1+4\nu_3^1$	0.00000921	0.68	
$4\nu_3^1$	0.000161	0.72	
$2\nu_1+3\nu_3$	0.00000921	0.82	
$\nu_1+3\nu_3^1$	0.000207	0.88	
$3\nu_3^1$	0.002303	0.945	1.26
$2\nu_1+2\nu_3^1$	0.0002533	1.13	
$\nu_1+2\nu_3^1$	0.00645	1.24	1.68
$2\nu_3^1$	0.1497	1.38	1.85
$2\nu_1+\nu_3^1$	0.0237	1.90	
$\nu_1+\nu_3^1$	0.5988	2.22	2.95
ν_3^1	23.03	2.72	3.72

Figure 3. Transmission spectra from untreated and treated fused SiO_2. Spectrum from treated specimen has been displaced 15 percent vertically upward for clarity.

3. Summary

We have shown that OH^- absorption bands in fused silica can be decreased and eliminated by an isotope exchange reaction with deuterium - the so-called deuterium treatment. This treatment does produce additional absorption bands at longer wavelengths (roughly 1.34 longer wavelength) associated with the OD^- ion. From measurements on a thoroughly treated sample, we found that at least 80% of the optical absorption at 1.3 μm in Suprasil II is due to the wing of the 1.38 μm OH^- absorption band. Further work should be done on improving the efficiency of the reaction and to check how stable it is. For example a window passing high power laser beams exposed to a moist atmosphere might reverse the process.

References

[1] Stone, J.; Burrus, C. A. Reduction of the 1.38 μm water peak in optical fibers by deuterium-hydrogen exchange. Bell System Technical Journal 59(8): 1541-1548; 1980 October.

[2] Kaiser, P; Tynes, A. R.; Astle, H. W.; Pearson, A. D.; French, W. G.; Jaeger, R. E.; Cherin, A. H. Spectral losses of unclad vitreous silica and soda-lime-silicate fibers. J. Opt. Soc. Am. 63: 1141; 1973.

The question was asked if the OH^- was introduced by the flame or the atmosphere. The author did not know. Also, a member of the audience stated that they had not seen the absorption at 1.3 μm reported by the authors in fused silica samples they had obtained. Reactive atmosphere processing (RAP) was suggested as the cost effective way to remove it, if it were present.